Problem Statement

Well-bonded CCM is desirable, but challenging
- Loose powder CCM is acceptable if stack experiences uniform compression
  
  BUT: cross-cell thermal gradients, warping of components, etc causes local variation  
  (MnCo)$_3$O$_4$ coating delamination and loss of electrical contact

441 stainless steel

Contact material (CCM)

LSCF cathode
YSZ electrolyte

Ni-YSZ anode

Bonding at 1000°C or less to avoid oxidation of steel

This is a low sintering/bonding temperature!!
- poor bonding
- incomplete sintering = reduced conductivity

Can we find a material reactive enough to bond at <1000°C but stable at 800°C operation?

Our work suggests that CCM composites is a valid concept to improve bonding without sacrifice electrical performance
Our Approach

Approach 1:
Select CCMs from cathode materials set
- Assess conductivity, sintering, CTE, reaction with LSCF and MCO
- Down-select most promising candidates and do ASR testing

Novel CCM-Composites Idea
Approach 2: Glass- CCM composite
Approach 3: Inorganic binders

In-situ assessment
- Electrochemical performance
- High-temperature delamination testing
Approach 1: Selection of pure conventional CCM
### Candidate Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Formula</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSCF</td>
<td>La0.6Sr0.4Co0.8Fe0.2</td>
<td></td>
</tr>
<tr>
<td>LSCuF</td>
<td>La0.8Sr0.2Cu0.9Fe0.1O2.5</td>
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</tr>
<tr>
<td>LSC</td>
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<tr>
<td>SSC</td>
<td>Sm0.5Sr0.5CoO3</td>
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</tr>
<tr>
<td>SBSC</td>
<td>SmBa0.5Sr0.5Co2O5</td>
<td></td>
</tr>
<tr>
<td>GSC</td>
<td>GdSrCo2O5</td>
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</tr>
<tr>
<td>LSM</td>
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<tr>
<td>LBC</td>
<td>LaBaCo2O5</td>
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<tr>
<td>YBC</td>
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<tr>
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<tr>
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<td></td>
</tr>
<tr>
<td>LNF</td>
<td>La0.98Ni0.6Fe0.4O3</td>
<td></td>
</tr>
<tr>
<td>LSN</td>
<td>La1.2Sr0.8NiO4</td>
<td></td>
</tr>
<tr>
<td>LSF</td>
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</tr>
<tr>
<td>LNC</td>
<td>La2Ni0.6Cu0.4O4</td>
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</tbody>
</table>

LSM, LNF, SSC, LSCF purchased from Praxair

All others synthesized by GNP

**CCM requirements:**
- good bonding
- high electronic conductivity
- good CTE match
- chemical compatibility with LSCF and \((\text{MnCo})_3\text{O}_4\)

**Approach:**
Select candidates from cathode literature
- high conductivity
- low sintering temperature
## Screening Summary

<table>
<thead>
<tr>
<th></th>
<th>Incipient Sintering Point (°C)</th>
<th>Shrinkage at 900°C</th>
<th>Shrinkage at 1000°C</th>
<th>CTE at 800°C</th>
<th>Reacts with MCO? 800°C 150h</th>
<th>Reacting with LSCO? 1000°C 10h</th>
<th>Conductivity of bulk dense pellet 800°C (S/cm)</th>
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</thead>
<tbody>
<tr>
<td>LSCF</td>
<td>637</td>
<td>2.7</td>
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<td>15.5</td>
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<td>NO</td>
<td>NO NO 201</td>
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<td>YES YES 260</td>
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<td>1.5</td>
<td>5.5</td>
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<td>YES</td>
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<tr>
<td>LSF</td>
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<td>0.9</td>
<td>13.3</td>
<td>NO</td>
<td>NO</td>
<td>NO NO 133</td>
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<td>2.4</td>
<td>14.6</td>
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<td>NO</td>
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</tbody>
</table>

The most promising candidates are:
- LSCF: good sintering and moderate conductivity
- LSCuF: very good sintering at 1000°C
- LSC and SSC: extremely high conductivity, moderate sintering
- MCO and Cr$_2$O$_3$ layers dominate ASR
- Composition of CCM may affect MCO properties and Cr$_2$O$_3$ growth rate
- NCC ASR too high and unstable
- All others acceptable

800°C in air

~500mA/cm$^2$
Post-Mortem Analysis of ASR Specimens

EDAX determination of interdiffusion

<table>
<thead>
<tr>
<th></th>
<th>CCM</th>
<th>LSCF</th>
<th>CCM</th>
<th>MCO</th>
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<tbody>
<tr>
<td>LSC</td>
<td>Minor Fe none</td>
<td>Minor Mn La, Sr</td>
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<td></td>
</tr>
<tr>
<td>SSC</td>
<td>Minor Fe Minor Sm none Sr</td>
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<td></td>
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<td>LSCF</td>
<td>N/A N/A none Fe</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>LSCuF</td>
<td>none Minor Cu none Minor Fe/Cu</td>
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<td></td>
<td></td>
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<tr>
<td>NCC</td>
<td>none none Minor Mn Minor Nd/Cu/Ce</td>
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</table>
Novel Composite CCM Concept

by adding
--glass
--inorganic binder

Provide bonding not only within the material but also at the interfaces

Conventional design: Sintering aid
Approach 2: Glass-CCM Composites

- Glasses with suitable thermal properties flow and wet the CCM, LSCF, and MCO surfaces upon 1000°C sintering
- Glass candidates chosen from the known SOFC sealing glasses
- Initial CCM candidates is LSM (high stability, good baseline)
LSM-SPG glass Composites

Spruce Pine Glass (SPG) used to assess optimal glass loading range

Minimal reaction at $\leq 10\text{wt\%}$ glass

Significant reaction at $\geq 25\text{wt\%}$ glass
LSM-SPG glass Composites

These observations suggest a trade-off between improved mechanical properties and decreased conductivity upon adding glass

→ Chose 5wt% as optimum glass loading for further work
SOFC Glass-CCM Composites

Candidates:
A: Schott G018-281
B: Schott G018-305
C: Schott G018-337
D: Schott G018-311
E: Schott GM31107
SEM-COM SCN-1
SEM-COM SCZ-8

Schott E and SCZ-8 are most promising candidates – less than 50% reduction of conductivity
Glass-CCM Sintering Behavior

Addition of glass improves sintering at 1000°C

<table>
<thead>
<tr>
<th>Glass identifier</th>
<th>CTE ($10^{-6}$/K)</th>
<th>Softening point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schott E</td>
<td>10.0</td>
<td>649</td>
</tr>
<tr>
<td>SCZ-8</td>
<td>9.5</td>
<td>837</td>
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</table>

- SCZ-8 remains intact
- minimal microstructure effect

Schott E - flows into LSM matrix
- increases grain growth

LSM/SCZ-8

LSM/Schott E
### Mechanical Properties and ASR

#### 1000°C Sintering
- Room temperature tests

#### Mechanical properties improved with glass addition

<table>
<thead>
<tr>
<th>CCM</th>
<th>Glass</th>
<th>Vickers Hardness (MPa)</th>
<th>Adhesion on LSCF (MPa)</th>
<th>Adhesion on 441 MCO (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSM</td>
<td>none</td>
<td>1931</td>
<td>3.9</td>
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<td>LSM</td>
<td>SCZ-8</td>
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<td>2.9</td>
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<td>LSM</td>
<td>Schott E</td>
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<td>4.8</td>
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<tr>
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<td>SCZ-8</td>
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<tr>
<td>SSC</td>
<td>Schott E</td>
<td>6006</td>
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<td></td>
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</table>

Addition of glass does not significantly increase ASR of CCM/Interconnect

#### 800°C in air
- ~500mA/cm²

- LSM/SCZ-8
- LSM/Schott E
- Good interfacial adhesion
- Minimal interdiffusion between LSM/Glass and MCO
In-Situ Button Cell Stability

- Glass-CCM does not degrade stability of LSCF cathode
- Minimal effect on initial performance
- Upcoming tests with MCO-coated 441 interconnect will assess effect of Cr and partial current collection area
Approach 3: CCM-Inorganic Binder Composites

Add inorganic binders to improve bonding
- Aremco aqueous binders, similar to binders for 552, 516 and other well-known SOFC sealants
  Alumino-silicates, Alumino-phosphates, Silicates

Challenges:
- Reactivity between CCM and Binder?
- Binder loading optimization: improved strength vs. percolation of conductive particles

Low temperature cure, no oxidation of stainless steel in processing
### CCM-Inorganic Binder Composites Screening

<table>
<thead>
<tr>
<th>Binder Type</th>
<th>Major Components</th>
<th>pH</th>
<th>React with LSM Powder?</th>
<th>React with SSC Powder?</th>
</tr>
</thead>
<tbody>
<tr>
<td>542</td>
<td>Al,P, minor Si</td>
<td>2.5</td>
<td>Slight</td>
<td>YES</td>
</tr>
<tr>
<td>794</td>
<td>Al,P</td>
<td>3</td>
<td>NO</td>
<td>YES</td>
</tr>
<tr>
<td>795</td>
<td>Al,Cl</td>
<td>3.5</td>
<td>NO</td>
<td>Slight</td>
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<tr>
<td>644A</td>
<td>Al</td>
<td>4</td>
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<td>NO</td>
</tr>
<tr>
<td>644S</td>
<td>Si</td>
<td>9</td>
<td>NO</td>
<td>NO</td>
</tr>
<tr>
<td>830</td>
<td>Si, minor S</td>
<td>11.4</td>
<td>NO</td>
<td>NO</td>
</tr>
</tbody>
</table>

Acidic binders completely dissolve SSC and attack LSM

Compatible binders screened for conductivity and downselected to:

- LSM-830
- SSC-830
- LSM-542
- LSM-644A
ASR of CCM-Inorganic Binder Composites

Best candidates (LSM 644A and LSM 830) show low, stable ASR on interconnect

Adhesion on MCO441 (Mpa)

<table>
<thead>
<tr>
<th></th>
<th>Adhesion</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSM</td>
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<tr>
<td>LSM830</td>
<td>1.1</td>
</tr>
<tr>
<td>LSM644A</td>
<td>1.6</td>
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Room-temperature adhesion - minimal improvement
In situ Button Cell stability

- Addition of 644A does not degrade performance or stability significantly
- Addition of 830 degrades performance; suspect interaction with LSCF cathode
- Upcoming tests with MCO-coated 441 interconnect will assess effect of Cr and partial current collection area

800°C in air
~300mA/cm²
Conclusions

Down-selected most promising conventional CCM materials
- LSCF, LSC, SSC, and LSCuF

Addition of glass improves room-temperature mechanical properties with minimal effect on electrochemical performance
- LSM/SCZ-8 better electrochemical performance
- LSM/Schott E better mechanical performance

Addition of 644A inorganic binder
- Minimal effect on electrochemical performance
- Bonding needs further improvement

Novel Composite CCM concept is promising. High temperature mechanical improvement needs to be demonstrated.
Future Directions

- In situ tests with MCO-coated 441 current collector
- Demonstrate improvement of high-temperature bonding
- Improve bonding for inorganic binder-CCM composites
- Develop composites with SSC or other high-conductivity oxide
- Composites with mixed bonding aids
Thanks to Joe Stoffa and Briggs White

This work was supported by the US DOE through project MSD-NETL-01

Contact Info

Mike Tucker  mctucker@LBL.GOV
800°C: LSC, SBSC, NCC, LSCMF, LSF
900°C: GSC, LSN, LSCuF
1100°C: LBC, YBC
Note CTE for interconnect and cell <14ppm/K
- Matched CTE is desirable
- High CTE does not disqualify candidate material
  - Thin, porous layer
Conductivity less than predicted by density - minimal sintering/particle necking or GB issue
Conductivity of Dense CCM

- Measured for dense bars
- Conductivity of porous CCM after bonding at 900-1000°C will be lower
Sintering Behavior

- Extent-of-sintering related to strength in the CCM layer
  (not necessarily related to bonding at the interface with neighbor layers)

- Only a few candidates display significant sintering in the 900-1000°C range
Reactivity with Neighbor Materials

Pellets of mixed MCO/CCM and LSCF/CCM
Reacted in air at: Operating conditions (800°C 120h) and Sintering conditions (1000°C 10h)

Most candidates were non-reactive with MCO, but reacted with LSCF
In all cases, reaction zone restricted to <40\,\mu m

→ reaction may be acceptable for
- thick LSCF layer
- electrically conductive reaction products